

ALLIED CHEMICAL CORPORATION

MEMORANDUM

June 20, 1977

TO: R. R. Lamonte

FROM: E. R. McCarthy

SUBJECT: Identification of Products Resulting From
Pyrolysis of VF_2 -HFIB Copolymers

Summary

Three samples were received for pyrolysis analysis. Each sample was heated to 650°F and 700°F and the products evolved were examined at each temperature. One of the samples was also burned in air. The only products, detected in significant amounts were carbon dioxide, hexafluoroisobutylene (HFIB), vinylidene fluoride (VF_2) and hydrogen fluoride (HF), the latter component evolved only from the unstabilized sample.

Introduction

Three samples were received for analysis. These were labeled as follows 504897-24A, 504897-24B and 504897-24C. We were asked to heat each of these samples at temperatures of 650°F and 700°F in air and to identify the pyrolysis gases evolved at one hour intervals for a period of six hours. Also we were asked to burn 504897-24A in air and to examine the gases. S/N 504897-24A was described as a low molecular weight CM-1 Polymer containing 2% CaO stabilizer. S/N 504897-24B corresponds to -24A which had been heated overnight to 300°C. S/N 504897-24C was described as a high molecular weight CM-1 Polymer containing no stabilizer.

Experimental

For the lower temperature pyrolysis experiments at 650°F and 700°F, about one half gram of sample was used. The sample was loaded into a glass tube which was then partially inserted into a furnace maintained at the appropriate temperature. The tube was equipped with a rubber septum for gas sampling purposes. At the one hour intervals the gases were sampled with a 10cc syringe. 10cc were injected into the cold inlet system of the MS 902 Mass Spectrometer and a mass spectrum immediately recorded. For the burning of 504897-24A, about one half gram of sample was loaded into a glass tube and then the contents were heated with a Meeker Burner flame. After burning, the combustion tube was connected to the inlet port of the mass spectrometer introduction system and the gas sampled.

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Results and Discussion

The results are presented in the following tables. The only gases detected in significant amounts were CO_2 , VF_2 , HFIB and HF. The molecular ion (m/e 44) was used to monitor CO_2 in the mass spectrum. For VF_2 , the molecular ion (m/e 64) was used. For HFIB, m/e 145 corresponding to loss of F from the molecular ion was used. HF was not observed directly but was inferred from the presence of SiF_3^+ (m/e 85). The ion corresponding to loss of F from the SiF_4 molecular ion (m/e 85) was used to monitor its concentration. The relative amounts values in the tables were taken directly from the mass spectrometer computer printout. These values are not quantitative because mass spectrometer response factors have not been incorporated into the data.

As can be seen from the data in the Tables CO_2 appears to be the main component formed in each sample. Also the stabilizer seems to be very effective; no HF is detected in -24A and -24B. (Samples -24A and -24B contain 2% CaO.) Also, we observed no detectable pressure increase on the gauge affixed to the combustion tube of the polymer conditioned overnight at 300°C. For -24A and -24C, about an atmosphere of pressure developed in the tube very quickly, when it was placed in the furnace. This pressure remained during the course of the six hours. The amount of HFIB relative to CO_2 was lower for sample -24B. After the six hours run, each tube contained a yellowish residue that had condensed onto the cooler region of the tube. This represents compound formation resulting from thermal cracking of the polymer chain. We did not analyze the yellow residue. It should be mentioned that no trace of the very toxic PFIB was observed in any of the samples. Trace amounts of higher molecular weight species were found, particularly in -24C; a peak at m/e 208 could represent a molecular ion corresponding to $[(\text{HFIB} + \text{VF}_2) - \text{HF}]^+$. Also a peak at m/e 182 could represent a four carbon heptafluoro species C_4HF_7^+ .

Recommendations

To obtain quantitative information concerning the gases evolved in this experiment, we recommend pyrolysis gas chromatography.

E. R. McCarthy
E. R. McCarthy

ERM/nag
Enclosures

cc A. R. Paterson
J. S. Smith
S. Chandrasekaran

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TABLE I
S/N 504897-24A

Temperature (°F)	Interval (Hours Expired)	Relative Amount		
		CO ₂	HFIB	VF ₂
650	1	100		
650	2	100		
650	3	100		
650	4	100	0.5	0.5
650	5	100	2	
650	6	100	2	0.1
700	1	43	1	.6
700	2	61	7	3
700	3	100	30	20
700	4	100	42	34
700	5	96	58	39
700	6	98	55	46

TABLE II

S/N 504897-24B

<u>Temperature</u> <u>(°F)</u>	<u>Interval</u> <u>(Hours Expired)</u>	<u>Relative Amount</u>		
		<u>CO₂</u>	<u>HF1B</u>	<u>VF₂</u>
650	1	100		
650	2	100	2	1
650	3	100	1	1
650	4	100	3	1
650	5	100	9	4
650	6	100	5	1
700	1	100		
700	2	100	1	
700	3	100	2	
700	4	100	3	1
700	5	100	7	2
700	6	100	8	2

TABLE III
S/N 504897-24C

<u>Temperature (°F)</u>	<u>Interval (Hours Expired)</u>	<u>CO₂</u>	<u>HF18</u>	<u>VF₂</u>	<u>HF</u>
650	1	70	4	3	
650	2	100	24	8	66
650	3	100	27	10	76
650	4	100	32	11	93
650	5	100	41	14	98
650	6	100	41	13	98
700	1	100	16	5	53
700	2	100	22	6	91
700	3	100	23	6	98
700	4	100	34	9	120
700	5	100	22	6	90
700	6	100	27	8	98

TABLE IV
S/N 504897-24A

<u>Temperature</u>	<u>Relative Amount</u>		
	<u>CO₂</u>	<u>HF1B</u>	<u>VF₂</u>
(Flamed with Meeker Burner)	100	63	28

1-6

QUANTITATIVE MEASUREMENT OF OFF-GASES FROM CM-1 POLYMER AT 345°C (650°F)

20 mgm samples of powder coating grade CM-1 powder were sealed into 1 1/2" long capillary tubes, sealed in air and heated in a G.C. probe at 650°F for up to 15 hrs. Then the capillary was broken inside the G.C. inlet port and the gases analyzed.

Results are as shown:

	<u>Heating Time</u>		
	<u>15 Mins.</u>	<u>30 Mins.</u>	<u>15 hrs.</u>
CO ₂	<u>45mgms</u> lb. polymer	45	90
VF ₂	<u>45 mgms</u> lb. polymer	45	90
HFIB	<u>270 mgms</u> lb. polymer	315	405

There were also detected much smaller amounts of a low boiling and a high boiling component in the off-gases.

Shelton



CORPORATE CHEMICAL RESEARCH LABORATORY

REQUEST FOR SERVICES

REQUESTER: FILL IN RED CAPTIONED ITEMS ONLY.

VISION SCD	LOCATION PTL	DEPARTMENT OR ROOM NO. 204	CCRL ANALYSIS NO. 2567
WITTED BY S Chandrasekaran	TEL. EXT. 3203	DATE 12 Aug '77	SAMPLE NO. 504897-24A
ACCOUNT CODES →	DIVISION	CONTROL CENTER -	REQUESTER PROJECT NO. →

VPLE DESCRIPTION AND REQUEST

- (1) S/N 504897-24A - is an HFIB/VF₂ copolymer ^{containing 2% CaO stabilizer} which upon heating to 650°F will decompose to CO₂, HFIB & VF₂.
- (2) Need to know g HFIB / g Polymer evolved after ^{3.43°C} 3.43°C

HAZARDOUS PROPERTIES (V AND DESCRIBE)

- TOXIC
FLAMMABLE
REACTIVE
OTHER

1, 2, 3, 4, 5, & 6 hr interval at 650°F in air.
(343°C)

(3) Est: Above determination will require 1 week.

ANALYST & DATE	OPERATION AND RESULTS			CHARGE
Paul Bergochi 15 Aug '77 206	Samples Exposed @ 340°-345° C for 15 min, 30 min, + 15 hrs.			
	15 min	30 min	(15 hrs.)	
	CO ₂ - $\frac{0.1 \text{ mg}}{\text{g}}$	$\frac{0.1 \text{ mg}}{\text{g}}$	$\frac{0.2 \text{ mg}}{\text{g}}$	
	VF ₂ - $\frac{0.1 \text{ mg}}{\text{g}}$	$\frac{0.1 \text{ mg}}{\text{g}}$	$\frac{0.2 \text{ mg}}{\text{g}}$	
	HFIB - $\frac{0.6 \text{ mg}}{\text{g}}$	$\frac{0.7 \text{ mg}}{\text{g}}$	$\frac{0.9 \text{ mg}}{\text{g}}$	
TOTAL CHARGE				

ALLIED CHEMICAL CORPORATION

MEMORANDUM

DATE: August 29, 1977

SUBJECT: CM-1 Off Gases

TO: Dr. R. R. Lamonte

On January 20, 1977 I wrote a memo to Mr. Jeff Buck stating that two coaters have complained about chest pains after coating with CM-1. Dr. Minhas has reported another instance where chest pains were encountered. Other coatings, also being applied at the same time could have been the cause of the problem.

We need to obtain information on the CM-1 off gases before we have a serious problem. Could you use this recent incident to get this work moving.

W. A. Miller

W. A. Miller

WAM:gp

cc: P. Minhas
M. B. Berenbaum